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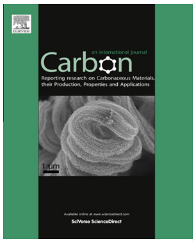

Spherical carbons: Synthesis, characterization and activation processes

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ABSTRACT

Spherical carbons have been prepared through hydrothermal treatment of three carbohydrates (glucose, saccharose and cellulose). Preparation variables such as treatment time, treatment temperature and concentration of carbohydrate have been analyzed to obtain spherical carbons. These spherical carbons can be prepared with particle sizes larger than 10 μm, especially from saccharose, and have subsequently been activated using different activation processes (H_3PO_4, NaOH, KOH or physical activation with CO_2) to develop their textural properties. All these spherical carbons maintained their spherical morphology after the activation process, except when KOH/carbon ratios higher than 4/1 were used, which caused partial destruction of the spheres. The spherical activated carbons develop interesting textural properties with the four activating agents employed, reaching surface areas up to 3100 m^2/g. Comparison of spherical activated carbons obtained with the different activating agents, taking into account the yields obtained after the activation process, shows that phosphoric acid activation produces spherical activated carbons with higher developed surface areas. Also, the spherical activated carbons present different oxygen groups' content depending on the activating agent employed (higher surface oxygen groups content for chemical activation than for physical activation).

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1. Introduction

Activated carbons (ACs) are very useful materials in environmental applications and new applications are emerging constantly, which implies that the world consumption of these materials is steadily increasing.

Morphology of the activated carbons is very important for their final applications and, in this sense, ACs can be prepared in different conformations such as powdered activated carbons (PACs) [1,2], granular activated carbons (GACs) [1,2], activated carbon fibers (ACFs) [3], carbon monoliths [4] or, very recently, spherical activated carbons [5,6].

Spherical activated carbons are receiving considerable attention for their various potential advantages over granular or powdered activated carbons such as high wear resistance, high mechanical strength, good adsorption performance, high purity, low ash content, smooth surface, good fluidity, good packaging, low pressure drop, high bulk density, high micropore volume and controllable pore size distribution [5,6]. Because of these advantages spherical activated carbons are being used in several applications such as blood purification, catalyst supports, in chemical protective clothing and others [6–8], and are attractive and potential materials for many adsorption processes, both in gas phase [9] and in solution [10].

For these reasons, an intense research has recently been carried out on the preparation of this type of materials using different experimental variables.

Regarding the precursors used, polymers are typically used for the preparation of spherical activated carbons. Two main

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types of polymers are often used: (i) spherical precursors derived from polymers such as divinylbenzene-derived spherical polymers [11] or polystyrene-based macroreticular ion-exchange resin spheres [12], or (ii) resins in powdered form such as phenol–formaldehyde resin [13] or urea/formaldehyde resin [14]. Some studies have also used mixtures of powdered activated carbons and resins as precursors [15].

Additionally, lignocellulosic materials have been object of great interest as precursors for the preparation of spherical activated carbons due to their low cost and for environmental concerns [16–26]. Among these lignocellulosic precursors, sugar cane [16], corn stover [20,23], rice straw [22], lettuce [24], or algae [25] can be mentioned.

Considering the advantages of lignocellulosic precursors, carbohydrates have also been recently selected as precursors for this application [27–36]. Lignocellulosic materials are composed by carbohydrates and, for this reason, the selection of the pure carbohydrates helps to better understanding the mechanism of formation of carbon spheres. Among the different carbohydrates, cellulose [22,26], glucose [33–35,37], fructose [38], saccharose [30,34,39], starch [28,34,40] or cyclodextrins [41] have been used.

Respect to the preparation of spherical activated carbons, several methods have been developed, which strongly depend on the precursor selected. In the case of polymeric precursors, polymerization reactions are used for the preparation of spherical carbons [14,42,43]. In the case of lignocellulosic materials and carbohydrates, hydrothermal treatment has been one of the preferred methods in recent years [17–19,20–26,44–46], although it is not a new method. The first research work on the hydrothermal treatment of carbohydrates was carried out during the first decades of the 20th century with the aim of understanding the mechanism of coal formation [47,48]. Wang et al. were the first to report the hydrothermal treatment of saccharose as a way to produce carbonaceous microspheres with sizes around 1.5 μm [18]. Later, Sun and Li reported on the preparation of carbonaceous microspheres of a tunable size (0.2–1.5 μm) from glucose or saccharose loaded with noble-metal nanoparticles by this method [37].

Since these first studies, the interest on the hydrothermal treatment for the preparation of spherical materials has been increasing along the years. As an example, Titirici et al. have been studying the preparation of spherical carbons from different biomass materials, such as sunflower stem, walnut shells or olive stones [49,50], or using different carbohydrates, such as monosaccharides (glucose [30,31,51] and xylose [20]), disaccharides (maltose [30] and saccharose [52]), polysaccharides (cellulose [50,53], potatoes starch [30] and amylopectin from potato starch [30]), or aldehydes, such as HMF and furfural, derived from thermal decomposition of carbohydrates [30,54]. These authors have analyzed the effect of different experimental variables such as hydrothermal treatment temperature, hydrothermal treatment time, type and concentration of carbohydrate and have deepen into the mechanism of formation of the spherical carbons by hydrothermal treatment [50,55].

However, although several authors have reported that hydrothermal treatment is a method to get a wide range of spherical carbon materials with controlled and functionalized structures (or nanostructures) from cheap and abundant precursors such as biomass and carbohydrates [34–46], few studies have analyzed the development of the porosity of the spherical carbons once the spheres have been prepared [50,53,56–59]. Thus, up to our knowledge, there were not published studies comparing the effect of the precursor and the activation method on the textural properties of the spherical activated carbons prepared, since in these previous studies the preparation of spherical activated carbons was only studied focusing on one activation method in each paper.

In this sense, the main aim of this paper is to study the preparation of spherical carbons by hydrothermal treatment of three carbohydrates with different structure, a monosaccharide (glucose), a disaccharide (saccharose) and a polysaccharide (cellulose), and, afterwards, to analyze the activation of these materials by several techniques, keeping the spherical morphology.

Regarding the hydrothermal preparation of spherical carbons, we have studied (i) how variables such as treatment time, treatment temperature and concentration of carbohydrates affect the spherical carbons formation and their properties and (ii) the effect of the precursor on the formation of spherical carbons. Regarding the activation to develop the adsorption capacity of these spherical carbons: (i) different activation methods have been analyzed (chemical activation with H_3PO_4, NaOH or KOH or physical activation with CO_2) and (ii) the effect of some variables such as the precursor, the activation method, the activating agent/precursor ratio (in chemical activation) or the activation time in physical activation (that leads to different burn-off percentages) on the textural properties of the prepared spherical activated carbons, has been deeply studied.

2. Experimental

2.1. Materials

Three pure carbohydrates have been used as precursors. The monosaccharide D-(+)-Glucose (GLU) has been supplied by Panreac Chemical, whereas the disaccharide D-(+)-Saccharose 98% (SAC) and the polysaccharide α-Cellulose (CEL) have been supplied by Sigma Aldrich.

2.2. Methods

2.2.1. Preparation of spherical carbons (SC) by hydrothermal treatment

The carbohydrates were mixed with 3.5 ml of distilled water to obtain molar concentrations of 0.8 and 1.6 M. Then, the mixture was put in a 10 ml capacity Teflon-lined stainless steel autoclave in a programmable oven, which was heated at different temperatures, 180, 200, 220, and 240 °C, during 24 h. Also, the time of hydrothermal treatment was varied between 12 and 48 h. The solid product was recovered by filtration, washed with distilled water and dried in an oven at 110 °C for 12 h.

In this section, the nomenclature of the different spherical carbons derived from carbohydrates is described as follows. In first place, the precursor is indicated (GLU for Glucose, SAC for Saccharose and CEL for Cellulose). In second place, the hydrothermal treatment is indicated (HT) and, in third place, the temperature, the time of thermal treatment or the concentration of carbohydrate are included.

2.2.2. *Activation processes of spherical activated carbons*

Spherical carbons obtained by hydrothermal treatment of the different precursors have developed their textural properties through chemical activation with H_3PO_4, NaOH or KOH or through physical activation with CO_2.

For H_3PO_4 activation, the method known as activation after incipient wetness impregnation, which was described in a previous work [60], was used. In this method, the samples were impregnated with a given H_3PO_4 solution by drop by drop addition to 1 g of sample with continuous stirring, until a small liquid film was formed at the surface. The volume to form a small liquid film was determined as 3.5 ml. The impregnated sample was then dried during 4 h at 110 °C. The H_3PO_4/precursor ratios used (1.7/1, 3.0/1, 4.1/1, and 5.0/1 $kg\,kg^{-1}$) were obtained using the constant H_3PO_4 solution volume (3.5 ml per gram of sample) and different H_3PO_4 concentrations (30, 50, 70, and 85 wt.%). Afterwards, the sample was activated in a horizontal quartz furnace tube 2 m long and 0.07 m diameter. In the activation process, 50 ml/min nitrogen flow was used, heating at 10 °C/min from ambient temperature to 450 °C, maintained for 1 h. The activated samples were finally washed with hot distilled water to eliminate any phosphoric acid residues.

NaOH and KOH activation methods were performed using a physical mixing method, in absence of water, between the precursor and activating agent, following the procedure described in previous works [61–64]. Thus, different amounts of activating agent, which is in form of lentils, were directly mixed at room temperature with 1.0 g of SC. In both cases, NaOH or KOH/precursor ratios of 2.0/1, 3.0/1, 4.0/1, and 5.0/1 were used. After physical mixing, the samples were carbonized in the same horizontal furnace described above. 200 ml/min nitrogen flow was used, heating at 5 °C/min from ambient temperature to 750 °C, maintained for 1 h.

In CO_2 activation method, a flow of 80 ml/min was used, heating at 10 °C/min from ambient temperature to 880 °C, and using activation times of 5, 10, and 15 h. The different activation times led to burn-off percentages of 60%, 75%, and 83% for spherical activated carbons obtained from GLUHT and 56%, 67%, and 81% for spherical activated carbons obtained from SACHT.

The nomenclature of the different spherical activated carbons can be described as follows. In first place, the precursor and the hydrothermal treatment are indicated (GLUHT, SACHT or CELHT), in second place, the activation methods (P for H_3PO_4, N for NaOH, K for KOH and C for CO_2) and, finally, in the case of the chemical activation, the activating agent/precursor ratio, and in CO_2 physical activation, the burn-off percentage.

2.2.3. *Characterization of SCs and spherical activated carbons*

2.2.3.1. *Morphological analysis*. Morphology of spherical carbons and spherical activated carbons was studied using scanning electron microscopy in a JEOL JSM-840.

2.2.3.2. *Porosity and surface chemistry*. The textural characterization of the SCs and spherical activated carbons was performed using N_2 adsorption at −196 °C and CO_2 at 0 °C [65,66], in a volumetric Autosorb-6B apparatus from Quantachrome. Before analysis, the samples were outgassed at 250 °C for 4 h. The BET equation was applied to the nitrogen adsorption data to get the apparent BET surface area (S_{BET}). The Dubinin–Radushkevich equation was applied to the nitrogen adsorption data to determine the total micropore volume (pores with size < 2 nm) and to the carbon dioxide adsorption isotherms to determine narrow micropore volumes (pores with size < 0.7 nm) [67]. Pore size distributions for all the spherical activated carbons were obtained applying the non-local density functional theory (NLDFT) to the N_2 adsorption data at −196 °C using the software provided by Quantachrome [68].

Temperature-programmed desorption (TPD) experiments were done in a DSC-TGA equipment (TA, SDT 2960 Simultaneous) coupled to a mass spectrometer (Balzers, OmniStar) to characterize the oxygen surface chemistry of all the samples [69]. In these experiments, 10.0 mg of sample were heated up to 950 °C (heating rate 20 °C/min) under a helium flow rate of 100 ml/min.

3. Results and discussion

3.1. *Preparation of SCs*

3.1.1. *Hydrothermal treatment temperature effect*

The study of the effect of the hydrothermal treatment temperature (180, 200, 220, and 240 °C) was performed on the three carbohydrates, keeping constant the treatment time (24 h) and the carbohydrate concentration (0.8 M). The change in morphology as a function of the temperature used can be observed in Fig. 1. The precursors (Fig. 1(a–c)) suffered changes in their morphologies after the hydrothermal treatment for all the temperatures employed, but in a different manner. Thus, microspheres were developed from 180 °C in two of the precursors, except in CEL, that required temperatures higher than 200 °C. Also, Fig. 1 shows that GLU and SAC developed spherical carbons with larger size than CEL in all the range of temperatures employed, and that SAC developed spherical carbons with the largest size when hydrothermal treatment was performed at 200 °C (Fig. 1h).

Due to our interest to obtain spherical carbons with large sizes, in the next section we analyze the effect of other variables (e.g., the time of hydrothermal treatment and the concentration of carbohydrate) on two selected precursors (GLU and SAC), because they both produced, at 200 °C, spherical carbons with the largest sizes.

3.1.2. *Hydrothermal treatment time effect*

For a fixed hydrothermal treatment temperature of 200 °C, using 0.8 M carbohydrate concentration, the hydrothermal time was studied. The times selected were 12, 24, and 48 h, as it is shown in Fig. 2. It can be observed that at 12 h spherical carbons have not well defined their morphology (Fig. 2(a and b)), whereas at larger times spherical carbons were obtained with defined morphology (Fig. 2(c–f). Because there were not significant differences between 24 and 48 h, the optimum preparation conditions were fixed at 200 °C and 24 h, for which spheres with sizes up to 4.7 μm were achieved, especially for spheres obtained from SAC.

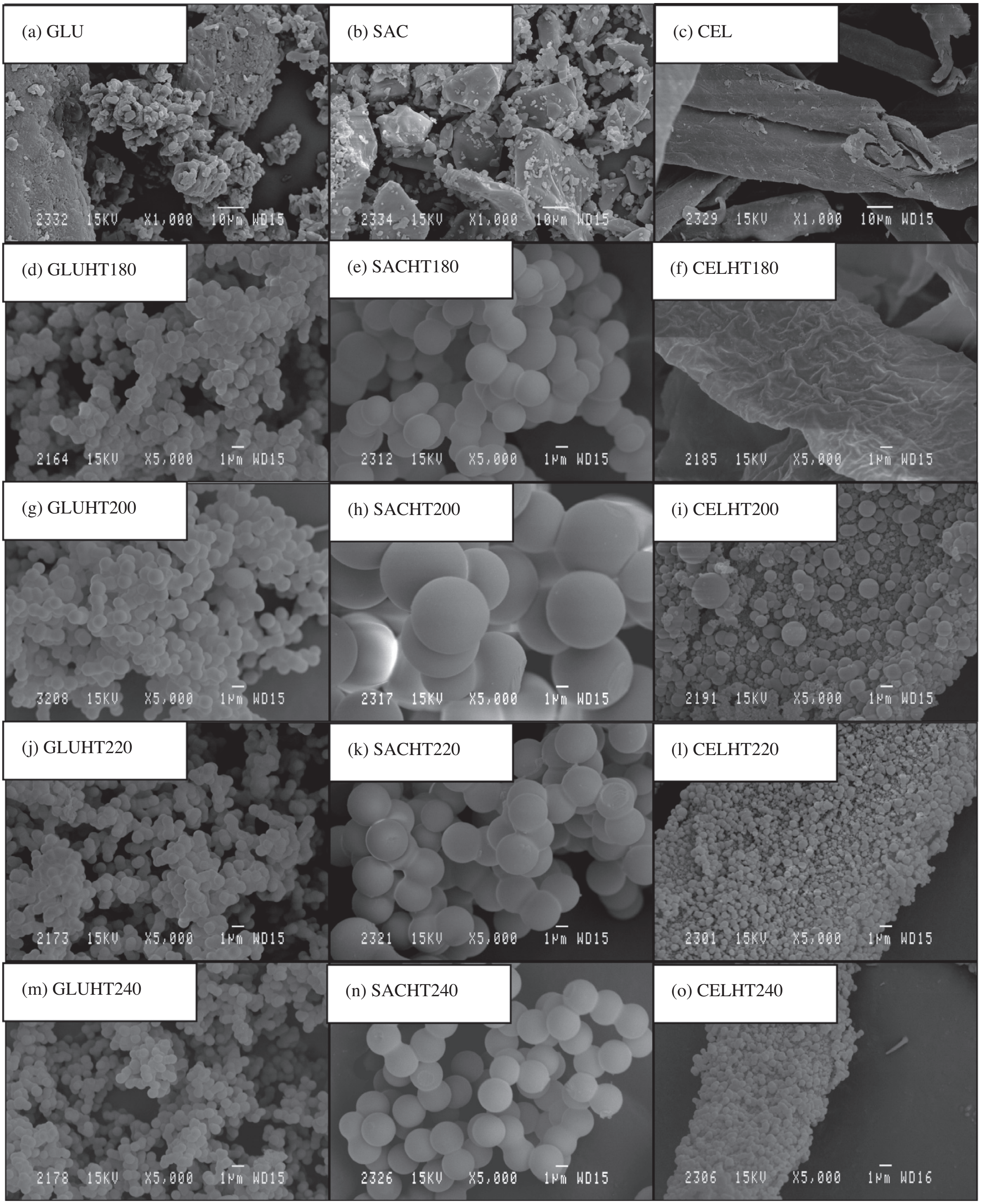
(a) GLU
2332 15KV X1,000 10µm WD15
(b) SAC
2334 15KV X1,000 10µm WD15
(c) CEL
2329 15KV X1,000 10µm WD15
(d) GLUHT180
2164 15KV X5,000 1µm WD15
(e) SACHT180
2312 15KV X5,000 1µm WD15
(f) CELHT180
2185 15KV X5,000 1µm WD15
(g) GLUHT200
3208 15KV X5,000 1µm WD15
(h) SACHT200
2317 15KV X5,000 1µm WD15
(i) CELHT200
2191 15KV X5,000 1µm WD15
(j) GLUHT220
2173 15KV X5,000 1µm WD15
(k) SACHT220
2321 15KV X5,000 1µm WD15
(l) CELHT220
2301 15KV X5,000 1µm WD15
(m) GLUHT240
2178 15KV X5,000 1µm WD15
(n) SACHT240
2326 15KV X5,000 1µm WD15
(o) CELHT240
2306 15KV X5,000 1µm WD16

Fig. 1 – SEM images of glucose, saccharose and cellulose before and after the hydrothermal treatment at different temperatures: (a), (b) and (c) precursors, (d), (e) and (f) at 180 °C, (g), (h) and (i) at 200 °C, (j), (k) and (l) at 220 °C, (m), (n) and (o) at 240 °C.

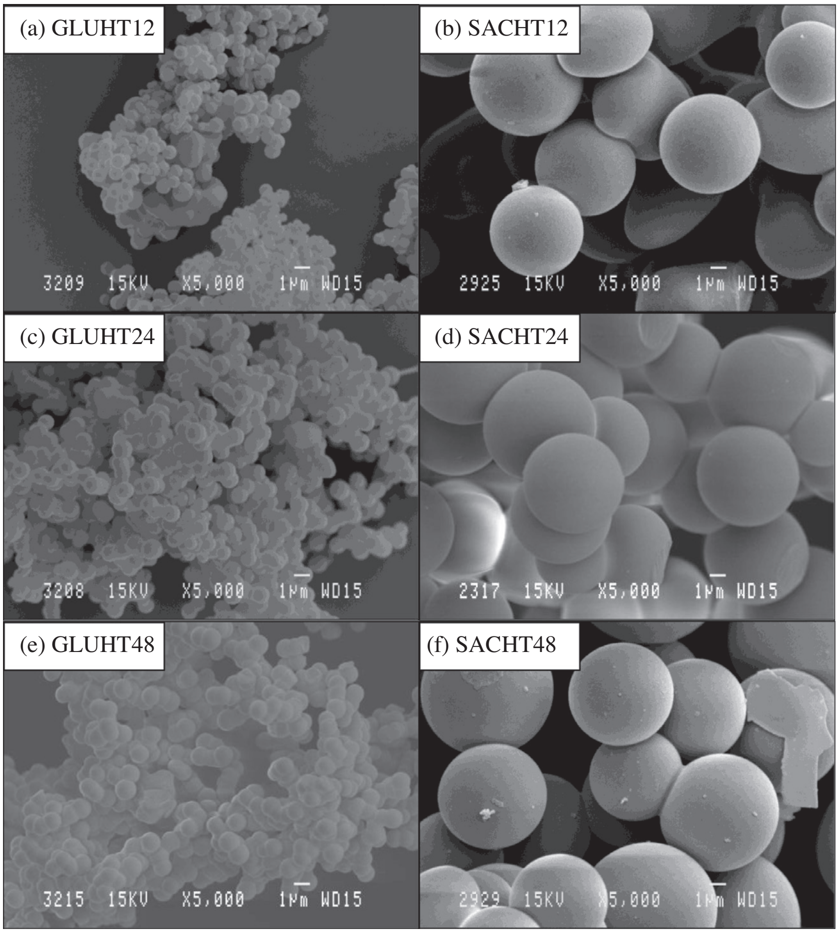
(a) GLUHT12
3209 15KV X5,000 1μm WD15
(b) SACHT12
2925 15KV X5,000 1μm WD15
(c) GLUHT24
3208 15KV X5,000 1μm WD15
(d) SACHT24
2317 15KV X5,000 1μm WD15
(e) GLUHT48
3215 15KV X5,000 1μm WD15
(f) SACHT48
2929 15KV X5,000 1μm WD15

Fig. 2 – SEM images of the spherical carbons obtained by hydrothermal treatment of GLU and SAC at different times: (a) and (b) at 12 h, (c) and (d) at 24 h, (e) and (f) at 48 h.

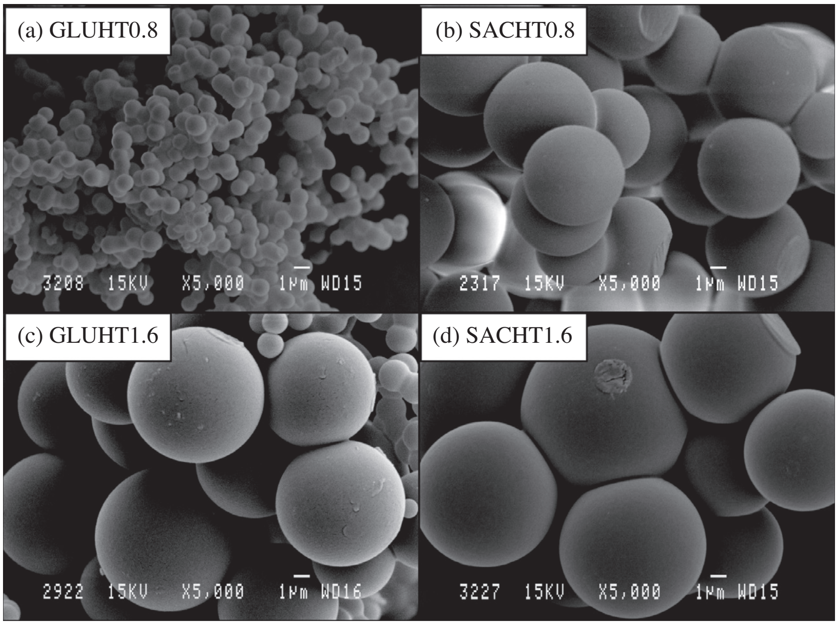
(a) GLUHT0.8
3208 15KV X5,000 1μm WD15
(b) SACHT0.8
2317 15KV X5,000 1μm WD15
(c) GLUHT1.6
2922 15KV X5,000 1μm WD16
(d) SACHT1.6
3227 15KV X5,000 1μm WD15

Fig. 3 – SEM images of the spherical carbons obtained by hydrothermal treatment of GLU and SAC at different concentrations: (a) and (b) 0.8 M concentration, (c) and (d) 1.6 M concentration.

3.1.3. *Carbohydrate concentration effect*

Concentration solutions of glucose and saccharose of 0.8 and 1.6 M were employed fixing the temperature and the time of the hydrothermal treatment at 200 °C and 24 h, respectively. Fig. 3 shows the results for the hydrothermal treatment of GLU and SAC. From it, the following observations can be extracted: (i) an increase in the concentration of carbohydrate produced an increase on the size of the spherical carbon prepared, (ii) the highest increase was observed for GLU and (iii) SAC always developed larger microspheres than GLU. Thus, at a concentration of 0.8 M the microspheres had an average size of 0.72 μm for GLU and up to 4.7 μm for SAC (Fig. 3a and b). At the concentration of 1.6 M, the mean size of the microspheres increased to 5.8 μm for GLU and to 12 μm for SAC.

3.2. *Activation processes for the preparation of spherical activated carbons*

Spherical activated carbons were prepared only from SCs obtained from glucose (GLUHT) and saccharose (SACHT), due to the mean size of the spheres obtained from these precursors were larger than those obtained from CEL. Different activating agents were used: H_3PO_4, NaOH, KOH or CO_2.

Due to the interest in maintaining the spherical form of the materials upon activation, we studied their morphology changes. Fig. 4 shows, for selected samples having similar textural properties, the morphology changes of GLUHT and SACHT activated with H_3PO_4, NaOH, KOH or CO_2. It should be noted that the activating agent/precursor ratios employed in this comparison were different depending on the activation method used: 1.7/1 in the case of H_3PO_4, 4/1 in the case of NaOH and KOH and a burn-off percentage of 80% for CO_2 activation.

From these figures we can conclude that all the materials maintained their spherical morphology after activation process. Only for a sample obtained with KOH at 4/1 ratio the spherical morphology was partially destroyed, as shown in Fig. 4(e and f)).

These observations show that 4/1 is a too high activation ratio for KOH. To confirm this, we have analyzed the morphology of spherical activated carbons at different activating agent/precursor ratios (2/1, 3/1, 4/1, and 5/1 KOH/precursor ratios) for GLUHT and SACHT. It can be concluded that for activating agent/precursor ratios lower than 4/1, spherical activated carbons maintain their spherical morphology, whereas for larger activating agent/precursor ratios, that is 4/1 and 5/1, their spherical morphology is, at least, partially destroyed.

3.2.1. *Textural properties of spherical activated carbons*

All the prepared spherical activated carbons were characterized by N_2 adsorption–desorption at −196 °C and CO_2 adsorption at 0 °C. Fig. 5 shows N_2 adsorption–desorption isotherms at −196 °C for spherical activated carbons obtained from GLUHT and SACHT by different activation methods. For a better comparison of the activation methods this figure presents samples with similar porosity developments, as Fig. 4. In summary, it is worth noting: (i) the marked microporous character (isotherms type I [70]) of the spherical activated carbons; (ii) that H_3PO_4 activation produces high porosity spherical activated carbons when SAC is selected as precursor, (iii) that NaOH or KOH lead to spherical activated carbons with high porosity, especially from GLU, (iv) that spherical activated carbons with similar porosities were obtained from GLU and SAC when CO_2 is employed, and (v) that spherical activated carbons with wide pore size distribution have been obtained with KOH activation.

3.2.1.1. *H_3PO_4 activation.* Table 1 compiles the results obtained by H_3PO_4 activation of both precursors (GLUHT and SACHT). This table includes, among others, the activation carbon yields and the data deduced from N_2 and CO_2 adsorption isotherms. From the nitrogen isotherms, the apparent BET surface areas and Dubinin–Radushkevich micropore volumes ($V_{DR}N_2$) were obtained. From CO_2 isotherms the narrow micropore volumes ($V_{DR}CO_2 < 0.7$ nm) can be calculated from Dubinin–Radushkevich equation. The volume of mesopores (2–20 nm, $V_{mesopores}$) was estimated as the difference between the volume (expressed as liquid) of N_2 adsorbed at $P/Po = 0.9$ and that adsorbed at $P/Po = 0.2$ [65].

Yields obtained in the activation processes have been calculated taking into account the yields obtained in hydrothermal treatment from GLU (44%) and SAC (42%). The resulting activation yields are around 30%, being very similar for both precursors. The activation yields are quite interesting considering that these spherical activated carbons have high adsorption capacities, above 1500 m^2/g, higher for spherical activated carbons obtained from SACHT. Sample SACHT/P/3.0 presents the maximum porosity development, S_{BET} of 2120 m^2/g, $V_{DR}N_2$ of 1.0 cm^3/g and $V_{DR}CO_2$ of 0.61 cm^3/g. The high development of the textural properties in these materials is very interesting. Thus, carbon spheres obtained after hydrothermal treatment have very low surface areas, 5.1 m^2/g for GLUHT precursor and 8.7 m^2/g for SACHT precursor. Also, Table 1 shows that mesopore volumes in all spherical activated carbons are low (<0.13 cm^3/g).

3.2.1.2. *NaOH and KOH activation.* Tables 2 and 3 summarize the textural properties of spherical activated carbons obtained by NaOH and KOH activation, respectively. Tables 2 and 3 show that the yields achieved in the process of activation with hydroxides are significantly lower than those obtained with H_3PO_4 activation, reaching maximum values up to 18% for low activating agent/precursor ratios. When the hydroxide/precursor ratio increases, the yield decreases. In fact, the yield for SACHT/N/5.0 sample has not been included because it was too low [71].

In general, Tables 2 and 3 show that for both chemical activating agents, spherical activated carbons have been obtained, presenting the materials prepared from GLUHT better textural properties than those obtained from SACHT. The increase in the activating agent/precursor ratio produces an improvement in the textural properties (S_{BET}, $V_{DR}N_2$, and $V_{DR}CO_2$) of the spherical activated carbons obtained from the two precursors, reaching values of surface areas up to 2129 m^2/g, $V_{DR}N_2$ of 0.83 cm^3/g and $V_{DR}CO_2$ of 0.57 cm^3/g for GLUHT/N/5.0 sample (sample obtained from GLUHT by NaOH activation), and values of surface areas up to 3152 m^2/g, $V_{DR}N_2$

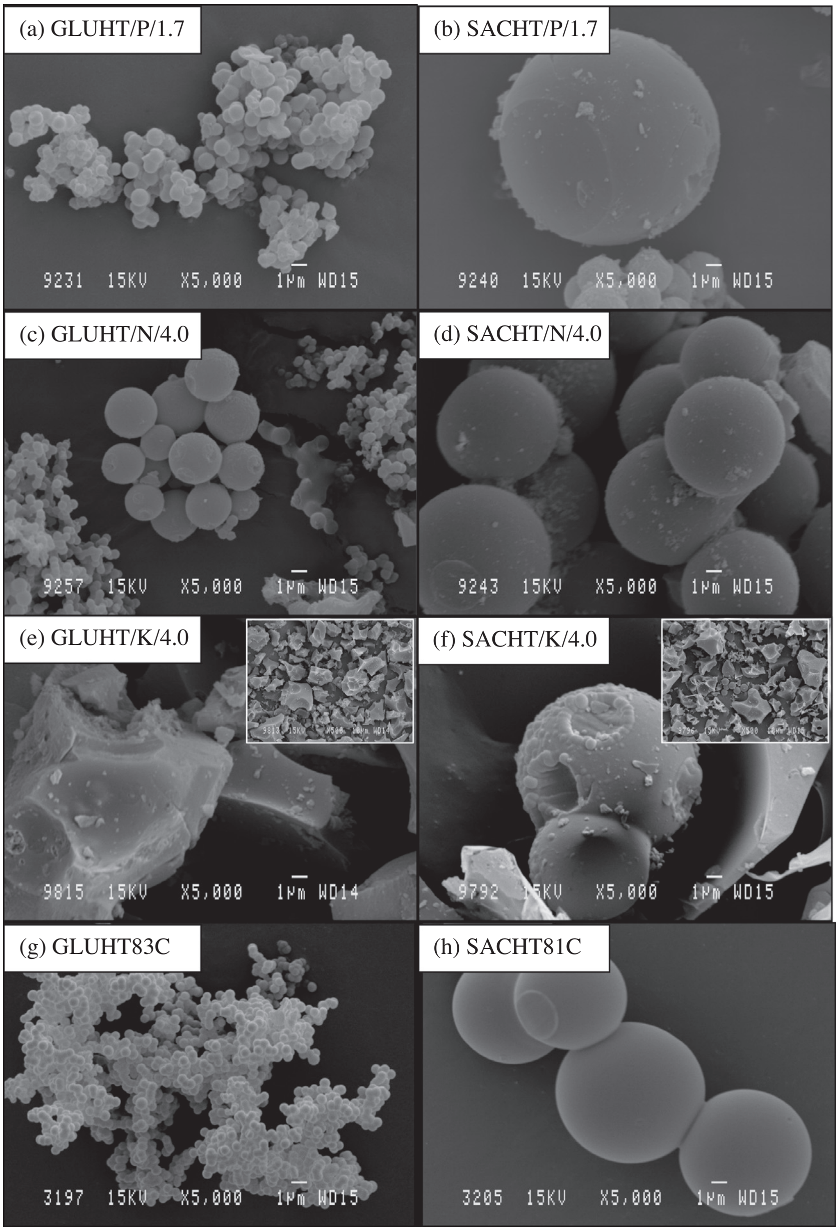
(a) GLUHT/P/1.7
9231 15KV X5,000 1μm WD15
(b) SACHT/P/1.7
9240 15KV X5,000 1μm WD15
(c) GLUHT/N/4.0
9257 15KV X5,000 1μm WD15
(d) SACHT/N/4.0
9243 15KV X5,000 1μm WD15
(e) GLUHT/K/4.0
9815 15KV X5,000 1μm WD14
(f) SACHT/K/4.0
9792 15KV X5,000 1μm WD15
(g) GLUHT83C
3197 15KV X5,000 1μm WD15
(h) SACHT81C
3205 15KV X5,000 1μm WD15

Fig. 4 – SEM images of the spherical activated carbons prepared with (a) and (b) H_3PO_4, (c) and (d) NaOH, (e) and (f) KOH, (g) and (h) CO_2.

of 1.18 cm^3/g and $V_{DR}CO_2$ of 0.70 cm^3/g for GLUHT/K/4.0 (sample obtained from GLUHT by KOH activation).

These results allow concluding that spherical activated carbons were prepared with controlled porosity. Thus, samples prepared with low activating agent/precursor ratios develop narrow microporosity (e.g., SACHT/N/2.0 sample has $V_{DR}N_2 = V_{DR}CO_2 = 0.22$ cm^3/g), whereas higher hydroxide/precursor ratios develop spherical activated carbons with micro and mesoporosity (e.g., mesopore volumes up to 0.57 cm^3/g for GLUHT/K/4.0 or 0.38 cm^3/g for GLUHT/N/5.0).

3.2.1.3. CO_2 *activation.*

Table 4 shows the textural properties of these spherical activated carbons obtained through CO_2 activation. It shows that obtained yields are lower than 18%, being similar to those obtained by NaOH or KOH activations.

From Table 4 it can be remarked that when the activation times are 5 h and 15 h, CO_2 activation allows obtaining, with the two precursors, spherical activated carbons with similar textural properties and with a homogeneous narrow microporosity distribution. Thus, as an example, samples SACHT56C and GLUHT60 (activation time of 5 h) have surface areas around 1000 m^2/g, whereas the samples SACHT81C and GLUHT83C have surface areas around 2500 m^2/g. However, at an activation time of 10 h, spherical activated carbons with different textural properties were obtained, presenting sample GLUHT75C much larger porosity development than SACHT67C.

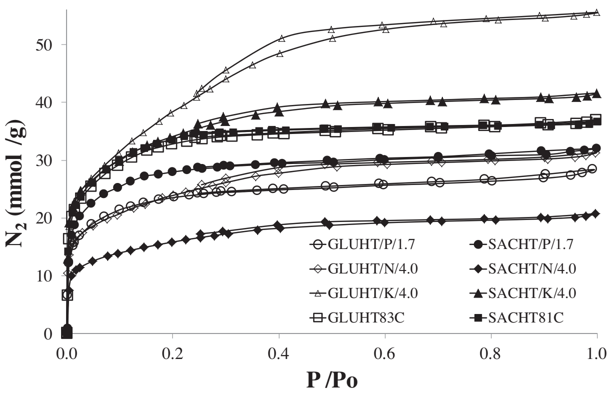

Fig. 5 – N_2 adsorption–desorption isotherms at −196 °C for spherical activated carbons obtained from both precursors, GLUHT and SACHT, by activation with H_3PO_4, NaOH, KOH or CO_2.

A comparison of the different activation methods used to develop textural properties of GLUHT and SACHT allows concluding that H_3PO_4 is the most effective activating agent because it develops high surface areas and provides higher activation yields. By contrast, NaOH is less effective activating agent because surface areas developed are moderate and provides lower yields.

Fig. 6 shows the analysis of the two parameters, surface area and yield (the product surface area·yield). From this figure we can conclude that: (i) H_3PO_4 is the best activating agent, e.g., SACHT/P/3.0, which has surface area of 2120 m^2/g and a yield of 29%, presents the greatest value of the product surface area·yield (615 m^2), being this product between 500 and 600 m^2 for most samples activated by phosphoric acid, (ii) KOH is the second most interesting activating agent, and the combination of high surface areas with low yield leads to values of the product surface area·yield around 300 m^2. For example, GLUHT/K/3.0, with a surface area of 2925 m^2/g and yield of 11%, has a product of 322 m^2, (iii) CO_2 is the following activating agent in these terms because its produces moderate surface areas and low yields. Thus, the product surface area·yield is in the range of 200 m^2 and (iv) NaOH is probably the less interesting activating agent because of low surface areas and low yields, leading to surface area·yield around 100 m^2 or less.

3.2.1.4. *Comparison of the spherical activated carbons obtained with those previously prepared in the literature.* The comparison of these results with those recently published is not easy due to the lack of publications dealing with the preparation and activation of spherical activated carbons by hydrothermal synthesis. The few publications dealing with similar objectives (the preparation and activation of spherical activated carbons through hydrothermal treatment) have not always been carried out under the same experimental conditions (carbon precursor, activation process, activating agent and/or experimental conditions) [50,53,56–58].

Falco et al. prepared spherical carbons by hydrothermal treatment from glucose, cellulose and rye straw, studying the effect of the hydrothermal treatment temperature on the formation of spherical carbons [53]. The spherical materials prepared were activated by KOH using a hydroxide/precursor ratio of 3/1 (weight terms) and the same temperature as the one employed in the present work (750 °C) [53]. The resulting activated carbons developed surface areas as high as 2250 m^2/g [53], which are somewhat lower than those reached in the present study (as high as 2925 m^2/g). Differences in the

Table 1 – Textural properties of spherical activated carbons obtained by H_3PO_4 activation.

Sample	Yield (%)	S_{BET} (m^2/g)	$V_{DR}N_2$ (cm^3/g)	$V_{DR}CO_2$ (cm^3/g)	$V_{mesopores}$ (cm^3/g)	CO_2 (μmol/g)	CO (μmol/g)	O^*(μmol/g)
GLUHT/P/1.7	31	1762	0.83	0.49	0.11	668	1809	3146
GLUHT/P/3.0	31	1750	0.80	0.46	0.11	296	1191	1873
GLUHT/P/4.1	32	1850	0.85	0.45	0.13	307	1283	1897
GLUHT/P/5.0	34	1493	0.66	0.36	0.11	539	1212	2290
SACHT/P/1.7	29	2100	0.99	0.60	0.11	320	1997	2638
SACHT/P/3.0	29	2120	1.00	0.61	0.10	288	2375	2951
SACHT/P/4.1	31	1824	0.81	0.45	0.12	404	1742	2551
SACHT/P/5.0	28	1776	0.86	0.48	0.10	957	5804	7719

[*] Total oxygen O = CO + $2CO_2$.

Table 2 – Textural properties of spherical activated carbons obtained by NaOH activation.

Sample	Yield (%)	S_{BET} (m^2/g)	$V_{DR}N_2$ (cm^3/g)	$V_{DR}CO_2$ (cm^3/g)	$V_{mesopores}$ (cm^3/g)	CO_2 (μmol/g)	CO (μmol/g)	O^* (μmol/g)
GLUHT/N/2.0	16	1098	0.45	0.35	0.10	905	1530	3340
GLUHT/N/3.0	11	1270	0.54	0.41	0.17	1607	2927	6141
GLUHT/N/4.0	7	1873	0.77	0.56	0.22	741	1867	3348
GLUHT/N/5.0	4	2129	0.83	0.57	0.38	1186	1756	4127
SACHT/N/2.0	16	532	0.22	0.22	0.05	1318	1115	3749
SACHT/N/3.0	12	855	0.35	0.29	0.11	1240	1765	4245
SACHT/N/4.0	7	1231	0.53	0.43	0.14	953	1420	4325
SACHT/N/5.0	–	–	–	–	–	–	–	–

[*] Total oxygen O = CO + $2CO_2$.

Table 3 – Textural properties of spherical activated carbons obtained by KOH activation.

Sample	Yield (%)	S_{BET} (m^2/g)	$V_{DR}N_2$ (cm^3/g)	$V_{DR}CO_2$ (cm^3/g)	$V_{mesopores}$ (cm^3/g)	CO_2 (μmol/g)	CO (μmol/g)	O^* (μmol/g)
GLUHT/K/2.0	18	1312	0.62	0.54	0.05	968	1404	3340
GLUHT/K/3.0	11	2925	1.17	0.71	0.25	890	2531	4309
GLUHT/K/4.0	8	3152	1.18	0.70	0.57	1075	1626	3775
GLUHT/K/5.0	7	2983	1.12	0.68	0.43	581	2458	3620
SACHT/K/2.0	15	1497	0.70	0.55	0.06	1007	1603	3616
SACHT/K/3.0	11	1643	0.77	0.60	0.06	679	1801	3158
SACHT/K/4.0	12	2662	1.13	0.76	0.23	709	1677	3095
SACHT/K/5.0	8	3136	1.21	0.74	0.42	758	1799	3316

[*] Total oxygen $O = CO + 2CO_2$.

Table 4 – Textural properties of spherical activated carbons obtained by CO_2 activation.

Sample	Activation time (h)	Yield (%)	S_{BET} (m^2 g^{-1})	$V_{DR}N_2$ (cm^3 g^{-1})	$V_{DR}CO_2$ (cm^3 g^{-1})	$V_{mesoporos}$ (cm^3 g^{-1})	CO_2 (μmol/g)	CO (μmol/g)	O^* (μmol/g)
GLUHT60C	5	18	1040	0.51	0.34	0.02	208	205	621
GLUHT75C	10	9	2077	0.98	0.64	0.14	399	233	1030
GLUHT83C	15	7	2499	1.12	0.70	0.14	317	456	1090
SACHT56C	5	18	923	0.45	0.44	0.01	290	100	680
SACHT67C	10	14	1202	0.59	0.53	0.02	375	394	1143
SACHT81C	15	8	2555	1.15	0.69	0.09	265	480	1010

[*] Total oxygen $O = CO + 2CO_2$.

hydrothermal treatment temperature of glucose might explain such difference.

Wisniewski et al. [56] studied the preparation of spherical activated carbons by hydrothermal synthesis performed on a saccharose solution (saccharose solution at 1 mol/L) in H_3PO_4, maintaining a molar ratio of activating agent/precursor ratio of 2/1 and hydrothermal-treatment temperature of 190 °C during 12 h. The spherical carbonized material obtained after the hydrothermal treatment was heat-treated at temperatures between 400 and 800 °C, obtaining spherical activated carbons with surface areas up to 2100 m^2/g [56]. This porosity development is similar to that of our sample SACHT/P/1.7 with a surface area of 2100 m^2/g, obtained with a lower activating agent/precursor ratio (1.7/1) and a lower activation temperature (450 °C).

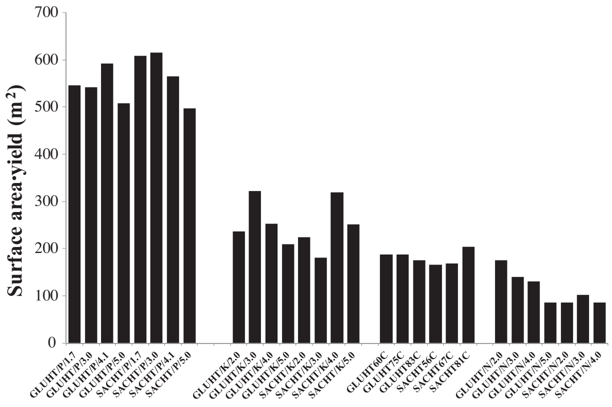

Fig. 6 – Comparison of the product surface area·yield obtained by activation with H_3PO_4, NaOH, KOH and CO_2.

Li. et al. studied the effect of the hydrothermal-treatment temperature (between 180 and 190 °C), hydrothermal treatment time (4–5 h) or concentration of glucose (0.3–0.5 mol/L) and the development of porosity by KOH activation [57]. The spherical activated carbons prepared at activating agent/precursor ratios of 4/1 and an activation temperature of 600 °C developed surface areas up to 1282 m^2/g and micropore volumes up to 0.44 cm^3/g. Their lower activation temperature (600 °C) can explain their lower activation results (our similar sample (GLUHT/K/3.0) prepared at 750 °C using a lower KOH/precursor ratio (3/1) has 2925 m^2/g) and the fact that their spheres are not destroyed using a 4/1 ratio, contrarily to our case.

Song et al. obtained spherical carbons by hydrothermal treatment of a glucose solution [58] and the activation was carried out by NaOH activation, but the results were quite low.

Román et al. prepared low-cost adsorbents with tunable surface chemistry by combination of hydrothermal carbonization and activation, either by air or CO_2 activation, using three precursors: walnut shell, sunflower stem and olive stone [59]. Their resulting materials can be considered as a mixture between activated carbons and spherical activated carbons, and present low surface areas (around 400 m^2/g).

From this limited comparison of the results reported in the literature and those obtained in the present work, we could notice some remarkable observations; (i) larger surface areas (values larger than 3100 m^2/g) are obtained in the present work, maintaining the spherical morphology and (ii) the selection of variables analyzed in this work (precursors, activating agents and preparation conditions) permits to prepare optimized spherical activated carbons with different porosities, porosity distributions (i.e., essentially microporous or with an important mesoporosity contribution) and different oxygen surface content, as it will commented next.

3.2.2. *Oxygen surface chemistry*

Surface chemistry content, especially the surface oxygen content, is important for the final application of the adsorbent (e.g., low surface oxygen groups' content would be suitable materials for their application in the adsorption of a non-polar VOC, such as toluene, at low concentration [9]). On the contrary, materials with high surface oxygen content would be interesting for their application in the adsorption of a polar VOC, such as formaldehyde, at low concentration [72].

Oxygen surface chemistry of the spherical activated carbons prepared through H_3PO_4, NaOH, KOH or CO_2 activation, has been characterized, and estimated, by Temperature-programmed desorption (TPD). Tables 1–4 show surface oxygen groups content for the spherical activated carbons obtained through the different activation methods. From comparison of these data it can be stated that chemical activation generates larger surface oxygen groups' content than CO_2 activation. The different activation methods lead to increasing total surface oxygen content in the following general order: $CO_2 < H_3PO_4 < KOH < NaOH$. However, the total oxygen groups content developed by CO_2 activation (which is low, around 1000 μmol/g), increases with the degree of activation.

Regarding chemical activation, the increase in the H_3PO_4 concentration, or the increase in the hydroxide/precursor ratio, does not have a clear influence on the total content of oxygen surface groups. However, it must be remarked that the sample activated from SAC by phosphoric acid at 5.0/1 ratio presents a very high surface oxygen groups' content, in the range of 8000 μmol/g, much larger than those for samples activated with phosphoric either with SAC precursor at lower ratios or with the GLU precursor.

4. Conclusions

Spherical carbons have been prepared from abundant and cheap precursors such as glucose, saccharose and cellulose, using a simple, economical and environmentally friendly method as hydrothermal synthesis.

The analysis of the effect of experimental variables such as the hydrothermal treatment temperature, hydrothermal treatment time and concentration of carbohydrate allowed to obtain spherical carbons from glucose and saccharose with interesting mean spherical sizes, that depend on the experimental conditions used for their preparation.

The carbohydrate concentration has shown to be the most important variable in the hydrothermal treatment of glucose and saccharose. The increase in the carbohydrate concentration leads to a considerable increase in the size of spheres, especially for those derived from glucose.

Spherical activated carbons were prepared from spherical carbons that had been previously obtained by hydrothermal treatment of glucose and saccharose. H_3PO_4, KOH, NaOH and CO_2 activation successfully developed the textural properties in these materials, maintaining the spherical morphology and reaching surface areas higher than 3100 m^2/g, micropore volumes up to 1.21 cm^3/g, narrow micropore volumes up to 0.76 cm^3/g or mesopore volumes up to 0.57 cm^3/g.

All spherical activated carbons prepared have to be analyzed besides their textural properties, from their variable surface oxygen chemistry content point of view, which is strongly dependent on the preparation method selected. These properties in all our materials make them very interesting for the adsorption of VOCs with different polarities at different concentration ranges.

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